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Patentanmeldung Nr. Patent application No. Demande de brevet n°

03029824.4

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(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
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One-part self-etching, self-priming dental adhesive composition

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One-part self-etching, self-priming dental adhesive composition

The present invention relates to a one-part self-etching, self-priming dental adhesive composition having a pH of at most 2, which contains a polymerizable phosphoric acid ester derivative and a further polymerisable acidic monomer. The polymerizable phosphoric acid ester derivative is resistant against hydrolysis in acidic medium.

Technical background

Presently, self-etching, self-priming dental adhesives are composed of two-part systems due to low hydrolysis stability of conventional polymerizable acidic ester monomers. The low hydrolysis stability arises from the hydrolysis of acidic and adhesive monomers in water or water/solvent mixtures. Therefore, the known acidic and adhesive monomers must be stored water-free and mixed with the aqueous part just before application.

Frequently, sulfuric acid ester and phosphoric acid ester groups are employed in acidic polymerizable adhesive monomers. However, these acidic groups hydrolyze the acrylic and methacrylic ester moieties as well as the phosphoric acid ester groups within the monomers (Moszner et al. *Macromol. Chem. Phys.* **2000**, 1062, (1999), DE 199 18 974, EP 1 169 996). In order to overcome these disadvantages, polymerizable phosphonic ester monomers were proposed by Moszner et al. (*Macromol. Chem. Phys.* **2000**, 1062, (1999), DE 199 18 974, and EP 1 169 996). Moreover, US. 4,539,382 discloses mono(meth)acrylamides with one phosphonic acid group. However, these monomers still comprise hydrolysable (meth)acrylic ester moieties. Therefore, monomers with phosphonic acid ester groups based on 2-(oxa alkyl) acrylate were suggested in DE 197 46 708. However, also these phosphonic acid derivatives tend to hydrolyse in acidic solution. Therefore, it has not been possible to provide a one-part self-etching, self-priming dental adhesive composition. A one-part composition means that the composition is contained in only one container which may be stored. It allows application of the composition without any mixing and without any special equipment before the application. Self-etching means that the dental adhesive composition may be applied to a tooth without any preliminarily etching of enamel in a separate method step. In order to provide a self-etching feature, the composition must be acidic. Self-priming means that the dental adhesive composition may be applied to a tooth without any preliminarily application of a primer.

In practice the monomers of the prior art could be employed only in two-part dental systems

which consist of a priming part and a bonding part. These two-part dental adhesive systems are either applied sequentially or in one step after mixing the two parts. Both procedures have inherent disadvantages due to clinical complications which might occur between sequential steps (saliva or blood contamination) or due to dosing problems when mixing is required prior to the application of the self-etching adhesive.

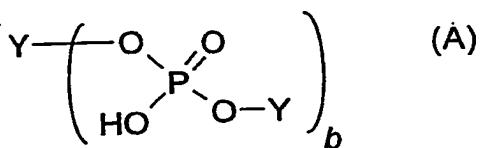
In order to overcome these clinical problems it is desired to provide a self-priming and self-etching adhesive as a one-part system eliminating the need of sequential application or premixing.

Further disadvantages of the monomers of the prior art containing phosphonic acid derivatives are as follows: The phosphonic acids are less acidic than phosphoric acid. Therefore, additional acids are required for obtaining the self-etching feature of a dental composition. However, the additional acid increases generally degradation of the monomer by hydrolysis. Moreover, the intermediates for producing the phosphonic acid derivatives are toxic. Therefore, the process for the preparation is dangerous and more complicated. Further, the phosphonic ester derivatives are more expensive than phosphoric acid derivatives.

Description of the invention

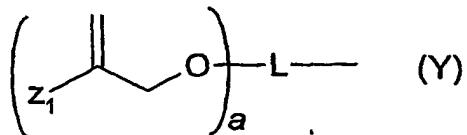
The above described needs and the disadvantages of the polymerizable phosphonic acid derivatives are solved by a one-part self-etching, self-priming dental adhesive composition having a pH of at most 2, which comprises

- (a) a polymerizable acidic phosphoric acid ester monomer of the following formula (A):



wherein

the moieties Y independent from each other represent a hydrogen atom or a moiety of the following formula (Y)



wherein

Z_1 is COOR^{10} , COSR^{20} , $\text{CON}(\text{R}^{10})_2$, $\text{CONR}^{10}\text{R}^{20}$, or CONHR^{10} , wherein R^{10} and R^{20} independently represent

a hydrogen atom,

a C_{1-18} alkyl group optionally substituted by a C_3 -cycloalkyl group,

an optionally substituted C_{3-8} cycloalkyl group,

an optionally substituted C_{4-18} aryl or heteroaryl group,

an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group, or

an optionally substituted C_{7-30} aralkyl group,

whereby two R_1 residues may form together with the adjacent nitrogen atom to which they are bound a 5- to 7 membered heterocyclic ring which may contain further nitrogen atoms or an oxygen atoms,

and whereby the optionally substituted groups may be substituted by 1 to 5 C_{1-5} alkyl group(s);

L represents an $(a+b)$ -valent organic residue (whereby b is 1 when Y is formula (A) is within the round brackets) containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including $a + b$ carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said $a+b$ carbon atoms linking a phosphate or 2-(oxa-ethyl)acryl derivative group;

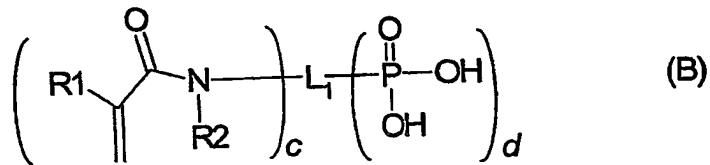
a is an integer of from 1 to 10, preferably 1 to 5;

b is an integer of from 1 to 10, preferably 1 to 5;

provided that at least one Y is not hydrogen; and

(b) one or more polymerisable acidic monomers selected from the group consisting of

(b1) polymerisable acidic monomers of the following formula (B):



wherein

R_1 and R_2 independently represent

a hydrogen atom,

an optionally substituted C_{1-18} alkyl group,

an optionally substituted C_{3-18} cycloalkyl group,

an optionally substituted C_{5-18} aryl or heteroaryl group,

an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group,

an optionally substituted C_{7-30} aralkyl group,

whereby the optionally substituted groups may be substituted by 1 to 5

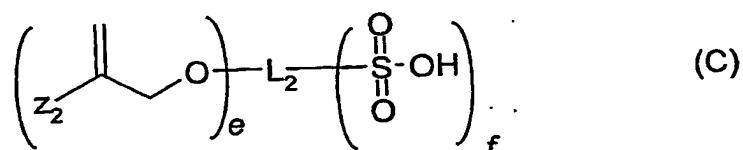
C_{1-5} alkyl group(s);

L_1 represents a $(c+d)$ valent organic residue containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur, the carbon atoms including $c+d$ carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said $c+d$ carbon atoms linking a phosphonate or optionally substituted acrylamido group;

and

c and d independently represent integers of from 1 to 10;

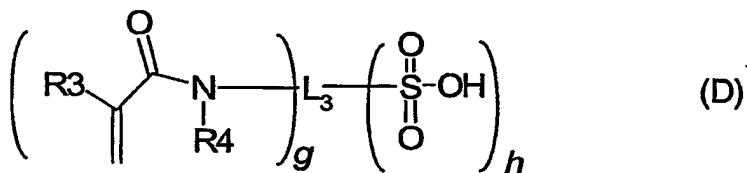
(b2) polymerisable acidic monomers of the following formula (C):



wherein

Z_2 independently has the same meaning as defined for Z_1 ;
 L_2 represents an $(e + f)$ valent organic residue containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including $e + f$ carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said $e+f$ carbon atoms linking a sulphonate or optionally substituted 2-(oxa-ethyl)acryl derivative group; and
 e and f independently represent an integer of from 1 to 10;

(b3) acidic monomers of the following formula (D):



wherein

R_3 and R_4 independently represent

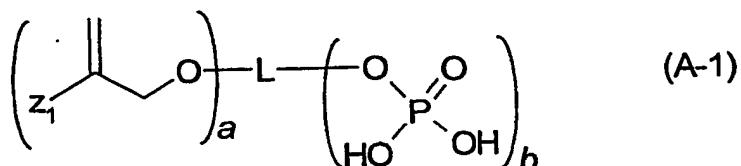
- a hydrogen atom,
- an optionally substituted C_{1-18} alkyl group,
- an optionally substituted C_{3-18} cycloalkyl group,
- an optionally substituted C_{5-18} aryl or heteroaryl group,
- an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group,
- an optionally substituted C_{7-30} aralkyl group,
- whereby the optionally substituted groups may be substituted by 1 to 5 C_{1-5} alkyl group(s)

L_3 represents a $(g + h)$ valent organic residue containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including $g + h$ carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said $g+h$ carbon atoms linking a sulphonate or optionally substituted acrylamido group; and

g and h independently represent integers of from 1 to 10;

- (c) a polymerizable N-substituted alkylacrylic or acrylic acid amide monomer;
- (d) an organic and/or inorganic acid;
- (e) an organic water soluble solvent and/or water; and
- (f) polymerization initiator, inhibitor and stabilizer.

In a preferred embodiment of the invention, the one-part self-etching, self-priming dental adhesive composition comprises a polymerizable acidic phosphoric acid ester monomer of the following formula (A-1):



wherein

Z_1 is COOR^{10} , COSR^{20} , $\text{CON}(\text{R}^{10})_2$, $\text{CONR}^{10}\text{R}^{20}$, or CONHR^{10} , wherein

R^{10} and R^{20} independently represent

- a hydrogen atom,
- a C_{1-18} alkyl group optionally substituted by a C_{3-8} cycloalkyl group,
- an optionally substituted C_{3-8} cycloalkyl group,
- an optionally substituted C_{4-18} aryl or heteroaryl group,
- an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group, or
- an optionally substituted C_{7-30} aralkyl group,

whereby two R^{10} residues may form together with the adjacent nitrogen atom to which they are bound a 5- to 7-membered heterocyclic ring which may contain further nitrogen atoms or an oxygen atoms,

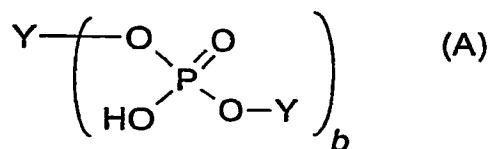
and whereby the optionally substituted groups may be substituted by 1 to 5 C_{1-5} alkyl group(s); L represents an $(a+b)$ -valent organic residue containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including $a + b$ carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said $a+b$ carbon atoms linking a phosphate or 2-(oxa-ethyl)acryl derivative group;

a is an integer of from 1 to 10, preferably 1 to 5;

b is an integer of from 1 to 10, preferably 1 to 5.

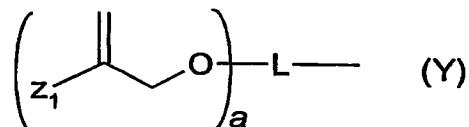
In a further preferred embodiment of the invention, the one-part self-etching, self-priming dental adhesive composition comprises a polymerizable acidic phosphoric acid ester monomer of formula (A) wherein none of the moieties Y is a hydrogen atom. In this case b is preferably an integer of from 1 to 5, more preferably of 1.

The present invention also provides a polymerizable acidic phosphoric acid ester monomer of the following formula (A)



wherein

the moieties Y independent from each other represent
a moiety of the following formula (Y)



wherein

Z_1 is COOR^{10} , COSR^{20} , $\text{CON}(\text{R}^{10})_2$, $\text{CONR}^{10}\text{R}^{20}$, or CONHR^{10} , wherein

R^{10} and R^{20} independently represent

a hydrogen atom,

a C_{1-18} alkyl group optionally substituted by a C_{3-8} cycloalkyl group,

an optionally substituted C_{3-8} cycloalkyl group,

an optionally substituted C_{4-18} aryl or heteroaryl group,

an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group, or

an optionally substituted C_{7-30} aralkyl group,

whereby two R_1 residues may form together with the adjacent nitrogen atom to which they are bound a 5- to 7-membered heterocyclic ring which may contain further nitrogen atoms or an oxygen atoms,

and whereby the optionally substituted groups may be substituted by 1 to 5 C_{1-5} alkyl group(s);

L represents an $(a+b)$ -valent organic residue (whereby b is 1 when Y in formula (A) is

within the round brackets) containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including a + b carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said a+b carbon atoms linking a phosphate or 2-(oxa-ethyl)acryl derivative group;

a is an integer of from 1 to 10, preferably 1 to 5;

b is an integer of from 1 to 10, preferably 1 to 5, more preferably 1.

Detailed Description of the Invention

In formula (A), the rest Z₁ may represent independently -COOR¹⁰, -COSR²⁰, -CON(R¹⁰)₂, -CONR¹⁰R²⁰, or -CONHR¹⁰. R¹⁰ and R²⁰ represent independently a hydrogen atom, a C₁₋₁₈ alkyl group optionally substituted by a C₃₋₈ cycloalkyl group, an optionally substituted C₃₋₈ cycloalkyl group, an optionally substituted C₄₋₁₈ aryl or heteroaryl group, an optionally substituted C₅₋₁₈ alkylaryl or alkylheteroaryl group, or

an optionally substituted C₇₋₃₀ aralkyl group, whereby two R¹⁰ residues may form together with the adjacent nitrogen atom to which they are bound a 5- to 7-membered heterocyclic ring which may contain further nitrogen atoms or an oxygen atoms, and whereby the optionally substituted groups may be substituted by 1 to 5 C₁₋₅ alkyl group(s). Examples for an alkyl group are methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, tert-butyl, pentyl, and hexyl. Examples for a cycloalkyl group are cyclopropyl, cyclobutyl, cyclopenty, and cyclohexyl. Examples for an aryl group are phenyl and naphtyl. Examples for a heteroaryl group are furyl and pyridyl. An example for an aralkyl group is benzyl.

In formula (A), L represents an (a+b)-valent organic residue containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including a + b carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said a+b carbon atoms linking a phosphate or 2-(oxa-ethyl)acryl derivative group. The organic residue L in the polymerizable phosphoric acid ester derivative of the present invention may contain further carbon, hydrogen, and hetero atoms, preferably oxygen and sulfur atoms, whereby oxygen atoms are particularly preferred. The number of the further atoms may vary and is not limited. According to a preferred embodiment of the present invention L may contain from 2 to 45, preferably up to 30, more preferably up to 18 and most preferably up to 10 carbon atoms. Also the number of further heteroatoms is not limited. According to a preferred embodiment of the

invention L may contain from 1 to 10 heteroatom(s), preferably oxygen atom(s). In a preferred embodiment of the invention the organic residue L is an (a+b)-valent saturated aliphatic C₂ to C₁₈ group having at least 2 of said primary aliphatic carbon atoms, and optionally 1 or more of said secondary aliphatic carbon atom(s), whereby said (a+b)-valent group may be substituted by C₁ to C₅ alkyl group(s); or a C₂ to C₄₅ mono-, di-, or polyether which has from 1 to 14 oxygen atoms and is substituted by at least 2 C₁ to C₁₀ aliphatic group(s) having said primary and/or secondary aliphatic carbon atoms; whereby said ether may optionally be substituted by C₁ to C₅ alkyl group(s). The number of such C₁ to C₅ alkyl group(s) may vary. Preferably, the ether may be substituted by 1 to 15, more preferably 1 to 5 C₁ to C₅ alkyl group(s).

According to a further preferred embodiment of the present invention, the organic residue L represents a saturated C₃ to C₈ cyclic, C₇ to C₁₅ bi- or polycyclic hydrocarbon group having from 0 to 4, preferably, 0 to 3, more preferably 0 or 1, of said secondary alicyclic carbon atoms; and/or a C₄ to C₁₈ aryl or heteroaryl group having from 0 to 5, preferably 0 to 3, more preferably 0 or 1, of said aromatic carbon atoms; whereby said saturated hydrocarbon or aryl or heteroaryl group is substituted by from 0 to 5 C₁ to C₅ alkyl group(s); from 0 to 4, preferably 1 to 3, more preferably 1 or 2, saturated C₁ to C₁₀ aliphatic group(s) having said primary and/or secondary aliphatic carbon atoms, and/or from 0 to 2 divalent residues according to one of the following formulas:

- [O-CH₂CH₂-]_f wherein f is an integer of from 1 to 10, preferably 1 to 5;
- [-O-CH₂CH₂CH₂-]_g] wherein g is an integer of from 1 to 10, preferably 1 to 5;
- [O-R₁₂]_h wherein R₁₂ is -CH(CH₃)-CH₂- or -CH₂-CH(CH₃)- and h is an integer of from 1 to 10, preferably 1 to 5;
- [-O-R₁₄]_i[-O-R₁₅]_j or -[-O-R₁₅]_k[-O-R₁₄]_l] wherein R₁₄ is -CH₂CH₂-, R₁₅ is -CH(CH₃)-CH₂- or -CH₂-CH(CH₃)-, i, j, k, and l are integers whereby
2i + 3j ≤ 15 and 2k + 3l ≤ 15,
- [O-CH₂CH₂CH₂CH₂-]_r wherein r is an integer of 1 or 2;

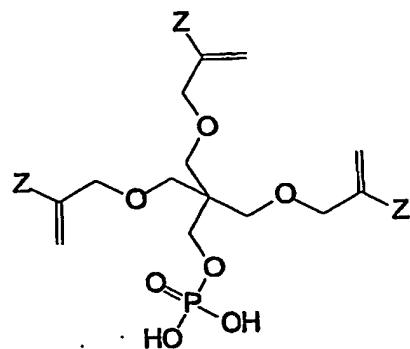
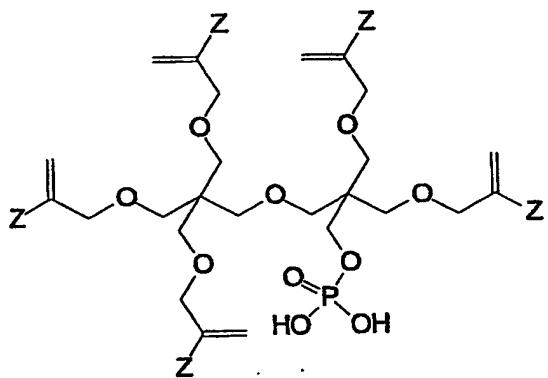
wherein said divalent residues have one of said primary aliphatic carbon atoms; and whereby 2 groups selected from said saturated hydrocarbon, aryl, and heteroaryl groups may optionally be linked by a single bond, an alkylene group, or -O-. Said alkylene group may be a C₁ to C₈ alkylene group. Preferably it is a C₁ to C₃ alkylene group, whereby an iso-propylene group is particularly preferred.

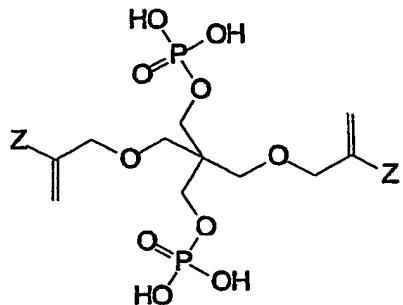
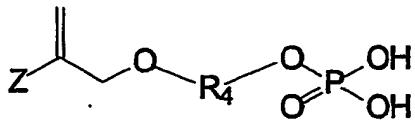
In a further embodiment of the present invention the organic residue L is an (a+b)-valent

saturated C₃ to C₈ cyclic or C₇ to C₁₅ bi- or tricyclic hydrocarbon group having at least 2 of said secondary alicyclic carbon atoms; an (a+b)-valent saturated C₅ to C₁₈ aryl or heteroaryl group having from 2 to 6 of said aromatic carbon atoms; an (a+b)-valent C₆ to C₁₈ alkylaryl or alkyl heteroaryl group having at least one of said aromatic carbon atoms, at least one of said secondary aliphatic carbon atoms, and optionally one of said primary aliphatic carbon atoms at the terminal end of the alkyl moiety of said alkylaryl or alkylheteroaryl group; or an (a+b)-valent C₈ to C₃₀ aralkyl group having at least one of said primary aliphatic carbon atoms and at least one of said secondary aliphatic carbon atoms.

In formula (A), *a* is an integer of from 1 to 10, preferably 1 to 5 and *b* is an integer of from 1 to 10, preferably 1 to 5.

Particularly preferred is the polymerizable phosphoric acid ester derivative which has one of the following formulas:





wherein

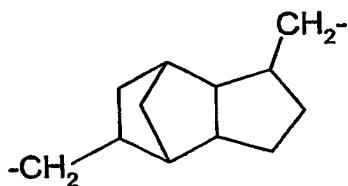
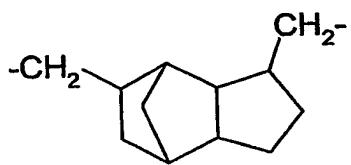
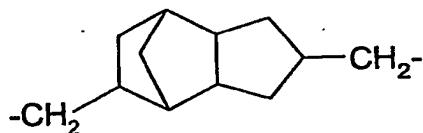
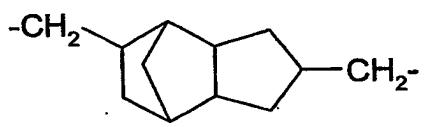
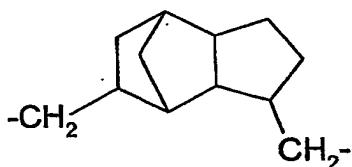
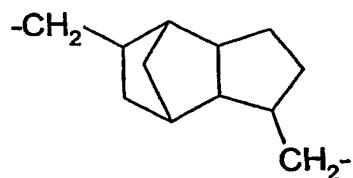
Z is Z_1 as defined above, R_4 denotes a divalent C_2 to C_{18} alkylene group, a divalent C_3 to C_8 cycloalkylene group, a divalent C_4 to C_{18} aryl or heteroaryl group, a divalent C_5 to C_{18} alkylaryl or alkylheteroaryl group, a divalent C_7 to C_{30} aralkyl group, whereby said groups may be substituted by 1 to 5 C_1 to C_5 alkyl group(s).

The polymerizable phosphoric acid ester derivatives in the above formulas have the advantage that a large number of polymerizable 2-(oxa-ethyl)acryl derivative groups and/or a large number of acidic phosphate groups are linked to one molecule. This allows to tailor the self-priming and self-etching features of a dental composition comprising such compounds. A large amount of polymerizable 2-(oxa-ethyl)acryl derivative groups per molecule enhances the bond strength of a dental adhesive composition comprising the polymerizable phosphoric acid ester derivative of the present invention. A large amount of phosphate groups per molecule enhances the self-etching feature of a dental composition comprising the polymerizable phosphoric acid ester derivative of the present invention. In a further embodiment of the present invention, the polymerizable phosphoric acid ester derivative has the above formula wherein R_4 is a divalent residue according to one of the following formulas:

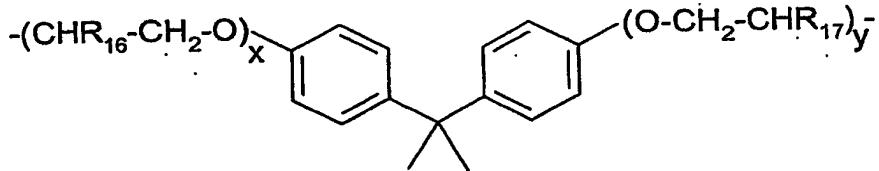
- $[\text{CH}_2\text{CH}_2-\text{O}]_m-\text{CH}_2\text{CH}_2-$ wherein m is an integer of from 1 to 14,

- $[\text{CH}_2\text{CH}_2\text{CH}_2-\text{O}]_p-\text{CH}_2\text{CH}_2\text{CH}_2-$ wherein p is an integer of from 1 to 14,

-[R₁₂-O]_q-R₁₃- wherein R₁₂ and R₁₃ may be -CH(CH₃)-CH₂- or
 -CH₂-CH(CH₃)- and q is from 1 to 14,
 -[R₁₄-O]_r-[R₁₅-O]_s-R₁₄- or -[R₁₄-O]_t-[R₁₅-O]_u-R₁₅- wherein R₁₄ is
 -CH₂CH₂-, R₁₅ is -CH(CH₃)-CH₂- or -CH₂-CH(CH₃)-, r, s, t, and u are integers thereby 2r + 3s
 ≤ 43 and 2t + 3u ≤ 42,
 -[CH₂CH₂CH₂CH₂-O-]_r-CH₂CH₂CH₂CH₂- wherein r is 1 or 2,



or



wherein R₁₆ and R₁₇ are H or -CH₃ and x and y may independently be integers of from 0 to 10, preferably 0 to 5.

Particularly preferred is the polymerizable phosphoric acid ester derivative as defined above, wherein said (a+b) carbon atoms are primary aliphatic carbon atoms.

The polymerizable phosphoric acid ester derivative of the present invention is hydrolysis stable under acidic conditions, preferably at a pH of at most 4, more preferably at a pH of at most 2, and most preferably at a pH of 1.0.

The one-part self-etching, self-priming dental adhesive composition of the invention comprises besides the polymerizable acidic phosphoric acid ester monomer of formula (A) one or more polymerisable acidic monomers selected from the group consisting of polymerisable acidic monomers of formula (B), (C) and (D):

In formula (B), R₁ and R₂ independently represent a hydrogen atom, an optionally substituted C₁₋₁₈ alkyl group, an optionally substituted C₃₋₁₈ cycloalkyl group, an optionally substituted C₅₋₁₈ aryl or heteroaryl group, an optionally substituted C₅₋₁₈ alkylaryl or alkylheteroaryl group, an optionally substituted C₇₋₃₀ aralkyl group, whereby the optionally substituted groups may be substituted by 1 to 5 C₁₋₅ alkyl group(s). Examples for an alkyl group are methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, tert-butyl, pentyl, and hexyl. Examples for a cycloalkyl group are cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. Examples for an aryl group are phenyl and naphtyl. Examples for a heteroaryl group are furyl and pyridyl. An example for an aralkyl group is benzyl.

In formula (B), L₁ represents a (c + d) valent organic residue containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur, the carbon atoms including c + d carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said c+d carbon atoms linking a phosphonate or optionally substituted acrylamido group. The organic residue L₁ in the polymerizable phosphonic acid derivative of the present invention may contain further carbon, hydrogen, and hetero atoms, preferably oxygen and sulfur atoms, whereby oxygen atoms are particularly preferred. The number of the further atoms may vary and is not limited. According to a preferred embodiment of the present invention L₁ may contain from 2 to 45, preferably up to 30, more preferably up to 18 and most preferably up to 10 carbon atoms. Also the number of further heteroatoms is not limited. According to a preferred embodiment of the invention L₁ may contain from 1 to 10 heteroatom(s), preferably oxygen atom(s).

In formula (B), c and d independently represent integers of from 1 to 10, preferably 1 to 5.

In formula (C), Z_2 may represent $-COOR^{10}$, $-COSR^{20}$, $-CON(R^{10})_2$, $-CONR^{10}R^{20}$, or $-CONHR^{10}$. R^{10} and R^{20} represent independently from formula (A) a hydrogen atom, a C_{1-18} alkyl group optionally substituted by a C_{3-8} cycloalkyl group, an optionally substituted C_{3-8} cycloalkyl group, an optionally substituted C_{4-18} aryl or heteroaryl group, an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group, or an optionally substituted C_{7-30} aralkyl group, whereby two R^{10} residues may form together with the adjacent nitrogen atom to which they are bound a 5- to 7-membered heterocyclic ring which may contain further nitrogen atoms or an oxygen atoms, and whereby the optionally substituted groups may be substituted by 1 to 5 C_{1-5} alkyl group(s). Examples for an alkyl group are methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, tert-butyl, pentyl, and hexyl. Examples for a cycloalkyl group are cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. Examples for an aryl group are phenyl and naphtyl. Examples for a heteroaryl group are furyl and pyridyl. An example for an aralkyl group is benzyl.

In formula (C), L_2 represents an ($e + f$) valent organic residue containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including $e + f$ carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said $e+f$ carbon atoms linking a sulphonate or optionally substituted 2-(oxa-ethyl)acryl derivative group. The organic residue L_2 in the polymerizable sulphonic acid derivative of the present invention may contain further carbon, hydrogen, and hetero atoms, preferably oxygen and sulfur atoms, whereby oxygen atoms are particularly preferred. The number of the further atoms may vary and is not limited. According to a preferred embodiment of the present invention L_2 may contain from 2 to 45, preferably up to 30, more preferably up to 18 and most preferably up to 10 carbon atoms. Also the number of further heteroatoms is not limited. According to a preferred embodiment of the invention L_2 may contain from 1 to 10 heteroatom(s); preferably oxygen atom(s).

In formula (C), e and f independently represent an integer of from 1 to 10, preferably from 1 to 5.

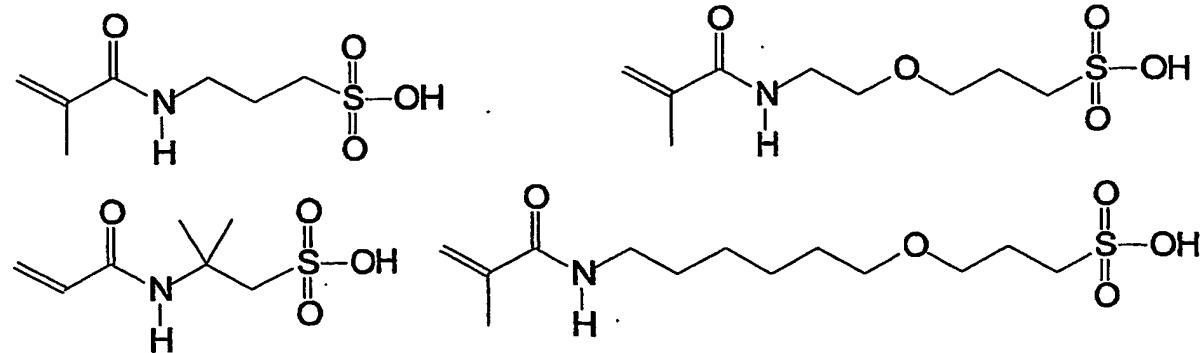
In formula (D), R_3 and R_4 independently represent a hydrogen atom, an optionally substituted C_{1-18} alkyl group, an optionally substituted C_{3-18} cycloalkyl group, an optionally substituted C_{5-18} aryl or heteroaryl group, an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group, an

optionally substituted C₇₋₃₀ aralkyl group, whereby the optionally substituted groups may be substituted by 1 to 5 C₁₋₅ alkyl group(s). Examples for an alkyl group are methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, tert-butyl, pentyl, and hexyl. Examples for a cycloalkyl group are cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. Examples for an aryl group are phenyl and naphtyl. Examples for a heteroaryl group are furyl and pyridyl. An example for an aralkyl group is benzyl.

In formula (D), L₃ represents a (g + h) valent valent organic residue containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including g + h carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said g+h carbon atoms linking a sulphonate or optionally substituted acrylamido group. The organic residue L₃ in the polymerizable sulphonic acid derivative of the present invention may contain further carbon, hydrogen, and hetero atoms, preferably oxygen and sulfur atoms, whereby oxygen atoms are particularly preferred. The number of the further atoms may vary and is not limited. According to a preferred embodiment of the present invention L₃ may contain from 2 to 45, preferably up to 30, more preferably up to 18 and most preferably up to 10 carbon atoms. Also the number of further heteroatoms is not limited. According to a preferred embodiment of the invention L₃ may contain from 1 to 10 heteroatom(s), preferably oxygen atom(s).

In formula (D), g and h independently represent integers of from 1 to 10, preferably from 1 to 5.

Preferably, the polymerizable monomer of formula (D) is characterized by one of the following formulas:



The polymerizable phosphoric acid ester derivative of the present invention has surprisingly high hydrolysis stability, although a phosphate group is present. Surprisingly, both the 2-(oxa-ethyl)-group and at the phosphoric acid ester group are hydrolysis stable under acidic conditions. Particularly, hydrolysis stability exists at a pH of at most 4, preferably at a pH of at most 2, most preferably at a pH of 1.0. Therefore, the polymerizable phosphoric acid ester derivative of the present invention allows the preparation of an advantageous one-pack self-etching and self-priming dental adhesive composition.

A one-pack composition means that the composition of the present invention is contained in only one container which may be stored and allows application of the composition without any mixing and without any special equipment before the application.

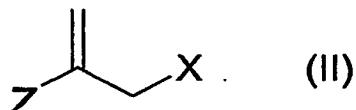
Self-etching means that the dental adhesive composition of the present invention may be applied to a tooth without any preliminarily etching of enamel in a separate method step. Particularly, the polymerizable phosphoric acid ester derivative of the present invention allows the preparation of a dental composition which is hydrolysis stable for at least one week at a storage temperature of 50 °C, whereby after such storage the bond strength of an adhesive prepared from such a dental composition to enamel and/or dentin is at least 10 MPa, preferably 15 MPa. Due to the high hydrolysis stability of the compound of the present invention a one-part self-etching and self-priming system which has excellent shelf-life may be prepared.

Further advantages of the polymerizable phosphoric acid ester derivative of the present invention are as follows: the phosphoric acid derivatives are stronger acidic than phosphonic acid derivatives.

A dental composition according to the present invention includes further acids whereby the pH of the composition may be easily adjusted. Surprisingly, neither the stronger phosphoric acid derivative of the invention nor additional acid(s) decrease the hydrolysis stability. Moreover, the intermediates for producing the phosphoric acid derivatives are not toxic. Therefore, the process for the preparation is safe, and the process for preparing the polymerizable phosphoric acid ester derivative of the present invention can be conducted more easily. Further, the phosphoric ester derivatives are generally less expensive than phosphonic acid derivatives.

The polymerizable phosphoric acid ester derivative of the present invention may be prepared by a process which comprises the following steps:

- (i) reacting a di- or polyol of the formula $(HO)_a-L-(OH)_b$ (I) with a compound of the formula (II):



wherein Z, L, a, and b are as defined above, particularly wherein L is R₄ as defined above, and

X is a leaving group for producing a compound (III) having b hydroxyl group(s) per molecule, and

- (ii) reacting compound (III) with a phosphoric acid derivative (IV) reactive with a hydroxyl group.

Preferably, the leaving group X is a halogen atom. Particularly preferred is that X is a chlorine or bromine atom, whereby a chlorine atom is most preferred.

The equivalent ratio between compound (II) and the di- or polyol (I) in the above process may be about a : 1. Further, the equivalent ratio between compounds (III) and (IV) may be b : 1 for preparing compounds of formula (A-1). If compound (III) is used in a higher equivalent amount (e.g. up to b:2), then phosphoric acid diesters will predominantly form. Preferably, the phosphoric acid derivative (IV) is phosphorus trichloride oxide. Moreover, the above described method may comprise hydrolyzing the reaction product of compounds (III) and (IV).

In case a polyol is used as compound (I), it may be advantageous that b hydroxyl groups of the polyol (I) are protected, then reacted with compound (II) followed by deprotecting before conducting step (ii). Any known protection agent for protecting hydroxyl groups may be used. Particularly preferred is 3,4-dihydro-2H-pyran, since it is suitable for primary, secondary and aromatic hydroxyl groups. Reacting 3,4-dihydro-2H-pyran with an alcohol under acidic conditions results in a tetrahydro-pyranylether which is stable under basic conditions and may be cleaved or deprotected easily with mild acids.

The dental composition of the invention may be an adhesive, a primer, a cement, a composite, etc. Particular preferred is a one-part self-etching, self-priming dental adhesive composition. The present invention provides a dental composition comprising a specific combination of polymerizable acidic monomers as described above and a polymerizable N-substituted alkylacrylic or acrylic acid amide monomer, an organic and/or inorganic acid, an organic water soluble solvent and/or water, and polymerization initiator, inhibitor and stabilizer. Preferably, components (a) and (b) are contained in a ratio of from 1:100 to 100 : 1.

The dental composition of the present invention has an acidic pH of at most 2, preferably a pH of about 1.0.

Moreover the dental composition of the present invention comprises a curing system. Such a curing system may comprises a polymerization initiator, an inhibitor and a stabilizer. The polymerization initiator may be a thermal initiator, a redox-initiator or a photo-initiator. Preferably, camphor quinone is used.

A stabilizer may be applied in order to stabilize the dental composition. Such a stabilizer may for example be a radical absorbing monomer, such as hydroquinone monomethylether, 2,6-di-tert-butyl-p-cresol, tetramethyl piperidine N-oxyl radical, galvanoxyl radical.

In a specific embodiment of the invention the dental composition may comprise a filler. This filler may be an inorganic filler and/or an organic filler. Preferably, the filler is a nanofiller.

Further, the dental composition of the present invention comprises an organic water soluble solvent and/or water. The organic water soluble solvent may be selected from alcohols, such as ethanol, propanol, butanol; and/or ketones such as acetone and methyl ethyl ketone. Particularly preferred is acetone, ethanol and/or tert-butanol.

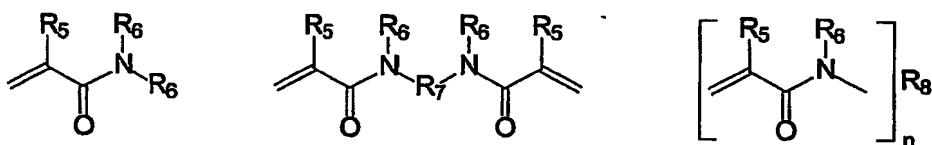
According to the present invention, the dental composition comprises an organic and/or inorganic acid. In a preferred embodiment, said organic acid of component (d) is selected from the group of mono- or polycarboxylic acids such as methacrylic acid, acrylic acid, fumaric acid, maleic acid, citric acid, itaconic acid, formic acid and wherein the inorganic acid of component (d) is selected from the group of ethylsulfonic acid, phosphoric acid, sulfuric

acid and hydrofluoric acid.

The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said acidic polymerizable monomer of component (b) is a polymerisable acidic monomers of formula (C).

The dental composition of the present invention also comprises a polymerizable N-substituted alkylacrylic or acrylic acid amide monomer.

Preferably, the polymerizable N-substituted alkylacrylic or acrylic acid amide monomer of component (c) is characterized by one of the following formulas:



wherein

R_5 and R_6 independently represent

- a hydrogen atom or a substituted
- a C_1 to C_{18} alkyl group,
- an optionally substituted C_{3-18} cycloalkyl group,
- an optionally substituted C_{5-18} aryl or heteroaryl group,
- an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group,
- an optionally substituted C_{7-30} aralkyl group, or two R_6 residues may form together with the N-atom to which they are bound a 5- to 7-membered heterocyclic ring which may contain beside said N-atom a further nitrogen atom or an oxygen atom, and whereby the substituted groups may be substituted by 1 to 5 C_1 to C_5 alkyl group(s);

R_7 represents a

- a divalent substituted or unsubstituted organic residue having from 1 to 45 carbon atoms, whereby said organic residue may contain from 1 to 14 oxygen and/or nitrogen atoms and is selected from a C_1 to C_{18} alkylene group wherein from 1 to 6 - CH_2 -groups may be replaced by a $-N-(C=O)-CR_9=CH_2$

group wherein R₉ is a hydrogen atom or a C₁ to C₁₈ alkyl group, a divalent substituted or unsubstituted C₃ to C₁₈ cycloalkyl or cycloalkylene group, a divalent substituted or unsubstituted C₄ to C₁₈ aryl or heteroaryl group, a divalent substituted or unsubstituted C₅ to C₁₈ alkylaryl or alkylheteroaryl group, a divalent substituted or unsubstituted C₇ to C₃₀ aralkyl group, and a divalent substituted or unsubstituted C₂ to C₄₅ mono-, di- or polyether group having from 1 to 14 oxygen atoms, in particular

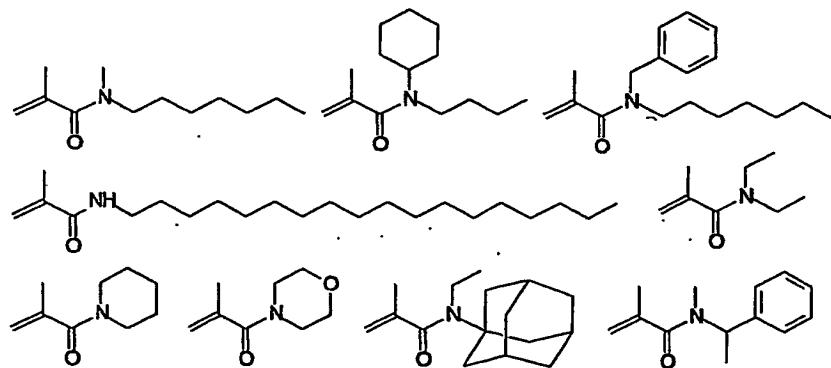
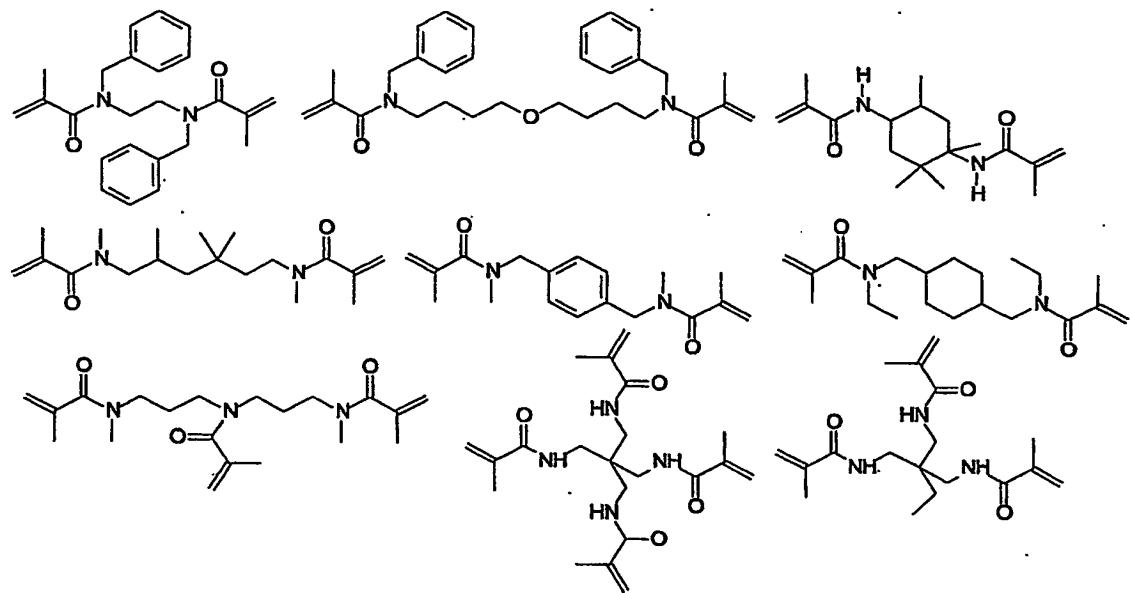
- an optionally substituted C₁₋₁₈ alkylene group,
- an optionally substituted C₃₋₁₈ cycloalkylene group,
- an optionally substituted C₅₋₁₈ arylene or heteroarylene group,
- an optionally substituted C₅₋₁₈ alkylarylene or alkylheteroarylene group,
- an optionally substituted C₇₋₃₀ aralkylene group,

R₈ represents

- a saturated di- or multivalent substituted or unsubstituted C₂ to C₁₈ hydrocarbon group, a saturated di- or multivalent substituted or unsubstituted cyclic C₃ to C₁₈ hydrocarbon group, a di- or multivalent substituted or unsubstituted C₄ to C₁₈ aryl or heteroaryl group, a di- or multivalent substituted or unsubstituted C₅ to C₁₈ alkylaryl or alkylheteroaryl group, a di- or multivalent substituted or unsubstituted C₇ to C₃₀ aralkyl group, or a di- or multivalent substituted or unsubstituted C₂ to C₄₅ mono-, di-, or polyether residue having from 1 to 14 oxygen atoms, in particular
- a di- or multivalent optionally substituted C₁₋₁₈ alkylene group,
- a di- or multivalent optionally substituted C₃₋₁₈ cycloalkylene group,
- a di- or multivalent optionally substituted C₅₋₁₈ arylene or heteroarylene group,
- a di- or multivalent optionally substituted C₅₋₁₈ alkylarylene or alkylheteroarylene group,
- a di- or multivalent optionally substituted C₇₋₃₀ aralkylene group, and

n is an integer, preferably from 2 to 10, more preferably from 3 to 4..

More preferably, the dental composition of the present invention contains a mono-, bis- or poly(meth) acrylamide monomer characterized by one of the following formulas:



The dental composition of the present invention is preferably a hydrolysis stable one-part self-etching, self-priming dental adhesive composition. Such a composition is

advantageously hydrolysis stable, e.g. for at least one week at a storage temperature of 50 °C, whereby after such storage the bond strength of an adhesive prepared from such a dental composition to enamel and/or dentin is at least 10 MPa, preferably 15 MPa. The dental composition may contain from 5 to 90 wt-% of the polymerizable phosphoric acid ester derivative according to component (a). In a preferred embodiment, said organic water soluble solvent of component (e) is selected from the group of alcohols and ketones such as ethanol, propanol, butanol, acetone, methyl ethyl ketone.

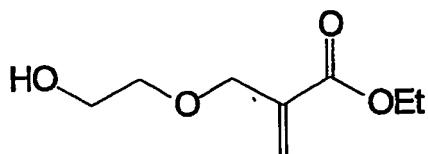
Preferably, the one-part self-etching, self-priming dental adhesive composition according to the invention contains said acidic polymerizable monomers of components (a) and (b) in an amount of from 5 to 90 wt-%. Said polymerization initiator is a thermal initiator, a redox-initiator or a photo initiator. The photo initiator may be champhor quinone. In the one-part self-etching, self-priming dental adhesive composition according to the invention, the filler may be an inorganic filler and/or an organic filler; preferably the filler is a nanofiller. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said stabilizer is a radical absorbing monomer such as hydroquinone, hydroquinone monomethylether, 2,6-di-tert.-butyl-p-cresol.

The present invention will now be explained in further detail by the following examples.

EXAMPLES

Example 1

Ethyl 2-[4-hydroxy-2-oxabutyl]acrylate (1)



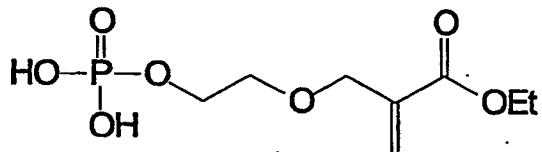
To a solution of 65.04 g trifluoromethanesulphonic acid anhydride in 240 ml dichloromethane

a solution of 30 g (0.230 mol) α -hydroxyethylacrylate and 23.33 g (0.230 mol) triethylamine in 450 ml dichloromethane was added slowly, so that the temperature of the reaction mixture stays below 5 °C. The solution was stirred for 75 min at 0 °C before it was added drop wise at room temperature to a solution of 70 g (1.127 mol) 1,2-ethandiol in 400 ml dichloromethane. After the reaction mixture was stirred for 14 h at room temperature the reaction was terminated by the addition of 500 ml of an aqueous sodium hydrogen carbonate solution (1n). The layers were separated and the organic fraction washed with 1 x 500 ml of an aqueous sodium hydrogen carbonate solution (1n) and 1 x 400 ml water. After the organic layer was dried over magnesium sulfate, filtered and evaporated, the oily residue was taken up in ethyl acetate and rinsed over a short silica gel column. After the evaporation of the solvent the oily raw product was stabilized with 15 mg BHT and purified by vacuum distillation (64 °C/0.04 mbar). This afforded 18.04 g (yield: 45 %) of a clear, colorless oil.
 IR(film, cm^{-1}) 3436 (OH), 2979, 2931, 2871 (CH_3/CH_2), 1710 (CO), 1638 (C=C), 1453, 1373, 1304 (CH_3/CH_2), 1270, 1173, 1109, 1052, 953.

$^1\text{H-NMR}$ (250 MHz, CDCl_3 , ppm) 1.27 (t, 3H, CH_3), 2.52 (broad s, 1H, OH), 3.54-3.63 (m, 2H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.67-3.78 (m, 2H, $\text{OCH}_2\text{CH}_2\text{O}$), 4.15-4.24 (m, 4H, CH_2 (1) and OCH_2CH_3), 5.84 (s, 1H, $\text{CH}=\text{C}$), 6.28 (s, 1H, $\text{CH}=\text{C}$).

$^{13}\text{C-NMR}$ (63 MHz, CDCl_3 , ppm) 14.06 (CH_3), 60.74 and 61.56 (CH_2 (4) and CH_2CH_3), 69.31 and 71.80 (CH_2 (1) and CH_2 (3)), 126.21 (C=C-CO), 137.03 (C=C-CO), 165.82 (C=C-CO).

Ethyl 2-[5-dihydrogen phosphoryl-5,2-dioxapentyl]acrylate (2)



To a stirred solution of 15.46 g (0.1008 mol) phosphorus oxychloride in 280 ml diethyl ether a solution of 17.56 g (0.1008 mol) 1 and 10.2 g (0.1008 mol) triethylamine in 250 ml diethyl ether was added dropwise, while the temperature was kept below 5 °C. After the reaction mixture was stirred for 14 h at room temperature, it was filtered and added slowly at 0 °C to 200 ml water. The emulsion was stirred for 40 min, before the layers were separated and the aqueous layer was washed with 2 x 100 ml diethyl ether. The aqueous layer was narrowed down to 100 ml and extracted with 4 x 100 ml dichloromethane. The organic fractions were

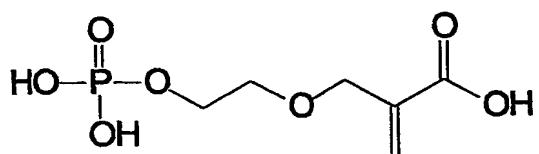
united, dried over magnesium sulfate, filtered and evaporated. This yielded 19 g of a yellow oil. The raw product was solved in 400 ml water and washed with 3 x 200 ml diethyl ether. Evaporation of the water at an rotary evaporator and drying under vacuum (10^{-3} mbar) afforded 14.18 g (yield: 55 %) of a clear colorless oil.

IR(film, cm^{-1}) 3500 – 2500 broad absorbtion (OH), 2912 (CH_3/CH_2), 1709 (CO), 1637 (C=C), 1456, 1374 (CH_3/CH_2), 1261, 1178, 1105, 1014, 949.

$^1\text{H-NMR}$ (250 MHz, CDCl_3 , ppm) 1.25 (t, 3H, CH_3), 3.70 (broad s, 2H, CH_2), 4.30 - 4.13 (m, 6H, CH_2), 5.87 (s, 1H, $\text{CH}=\text{C}$), 6.27 (s, 1H, $\text{CH}=\text{C}$), 10.71 (broad s, 2 H, PO_3H_2).

$^{13}\text{C-NMR}$ (63 MHz, CDCl_3 , ppm) 13.94 (CH_3), 60.94 (OCH_2CH_3), 66.01 (CH_2 (4)), 69.25 (CH_2 (1)), 69.40 (CH_2 (3)), 127.11 (C=C-CO), 136.28 (C=C-CO), 166.00 (C=C-CO).

2-[5-dihydrogen phosphoryl-5,2-dioxapentyly] acrylic acid (3)



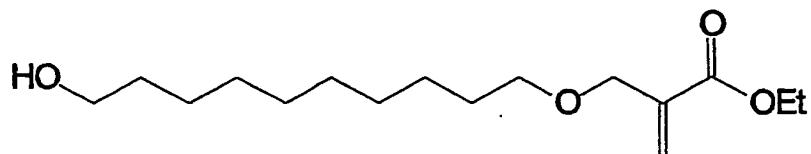
A solution of 7.08 g (0.0278 mol) **2** in 40 ml water was added to a solution of 7.88 g (0.197 mol) sodium hydroxide in 70 ml water, so that the temperature of the reaction mixture stays below 20 °C. The solution was stirred for 23 h at 23 °C, before it was washed with 2 x 200 ml diethyl ether and 1 x 100 ml dichloromethane. The aqueous layer was acidified by the addition of 40 ml of an aqueous hydrochloric acid (5 n), while the temperature of the solution was kept below 20 °C. The aqueous solution was washed with 4 x 100 ml dichloromethane and 1 x 100 ml diethyl ether, was saturated with sodium chloride and extracted with 1 x 200 ml acetonitrile and 3 x 200 ml tetrahydrofuran. The acetonitrile and tetrahydrofuran fractions were united, dried over magnesium sulfate, filtered and evaporated. This yielded a slightly reddish oil, which was solved in 200 ml water and washed with 3 x 200 ml diethyl ether. Evaporation of the aqueous layer and drying under vacuum (10^{-3} mbar) afforded 5.78 g (yield: 91 %) of a clear, yellow oil.

IR(film, cm^{-1}) 3500 – 2500 broad absorption (OH), 2879 (CH_3/CH_2), 1693 (CO), 1630 (C=C), 1446 (CH_3/CH_2), 1104, 966, 826, 772.

$^1\text{H-NMR}$ (250 MHz, d_6 -DMSO, ppm) 3.56 (m, 2H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.92 (m, 2H, $\text{OCH}_2\text{CH}_2\text{O}$), 4.08 (s, 2H, CH_2 (1)), 5.76 (s, 1H, $\text{CH}=\text{C}$), 6.09 (s, 1H, $\text{CH}=\text{C}$), 10.65 (broad s, 3 H, PO_3H_2 , CO_2H).
 $^{13}\text{C-NMR}$ (63 MHz, d_6 -DMSO, ppm) 65.12 (CH_2 (4)), 69.07 (CH_2 (1)), 69.87 (CH_2 (3)), 125.51 (C=C-CO), 138.36 (C=C-CO), 167.35 (C=C-CO).

Example 2

Ethyl 2-[12-hydroxy-2-oxadodecyl]acrylate (1)



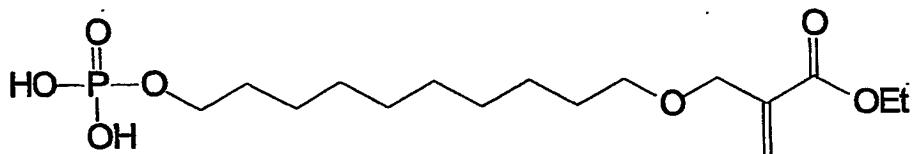
To a stirred solution of 10 g (57.4 mmol) 1,10-decandiol and 5.86 g (57.90 mmol) triethylamine in 100 ml tetrahydrofuran 8.50 g (57.20 mmol) ethyl α -chloromethylacrylate were added at room temperature. The reaction mixture was refluxed for 40 h. The reaction mixture was cooled down to room temperature and the developing precipitate was filtered off. Evaporation of the filtrate afforded a mixture of a clear, yellow oil with a white solid. This mixture was taken up in a small amount of dichloromethane and filtered again. The filtrate was solved in 150 ml dichloromethane and washed twice with 50 ml water. The organic layer was dried over magnesium sulfate the reaction mixture, filtered and evaporated. The raw product was purified by column chromatography on silica gel with dichloromethane and ethyl acetate as eluens. This afforded 6,37 g (yield: 38,9 %) of a clear, yellowish oil.

IR(film, cm^{-1}) 3425 (OH), 2926/2855 (CH_3/CH_2), 1714 (CO), 1638 (C=C), 1459/1375/1303 (CH_3/CH_2), 1270/1172/1102/1031/949.

¹H-NMR (250 MHz, CDCl₃, ppm) 1.08-1.24 (m, 15H, CH₂,CH₃), 1.24-1.49 (m, 4H, CH₂), 3.17 (broad s, 1H, OH), 3.27 (t, 2H, OCH₂) 3.37 (t, 2H, OCH₂), 3.96 (s, 2H, CH₂(1)), 4.01 (q, 2H, OCH₂CH₃) 5.65 (s, 1H, CH=C), 6.07 (s, 1H, CH=C).

¹³C-NMR (63 MHz, CDCl₃, ppm) 13.64 (CH₃), 25.36, 25.68, 28.98, 29.07, 29.11, 19.17 and 32.24 (CH₂(4-11)), 60.10 and 61.90 (CH₂(12) and CH₂CH₃), 68.31 and 70.52 (CH₂(1) and CH₂(3)), 124.69 (C=C-CO), 137.12 (C=C-CO), 165.37 (C=C-CO).

Ethyl 2-[13-dihydrogen phosphoryl-13,2-dioxatridecyl]acrylate (2)



To a stirred solution of 3.21 g (20.94 mmol) phosphorousoxytrichloride in 50 ml diethylether a solution of 5 g (17.45 mmol) 1 and 2.22 g (20.94 mmol) triethylamine in 50 ml diethylether was added dropwise, while the temperature was kept at 0 °C. After the addition was finished the reaction mixture was stirred for 0.5 h at 0 °C and for 16 h at room temperature before the reaction was finished by filtration of the suspension and evaporation of the solvent. The oily residue was solved in 100 ml diethylether and added dropwise to 100 ml water, while the temperature was kept at 0 °C. The layers were separated and the organic solution was washed successively with 50 ml of an aqueous sodium hydroxide (25 wt%) solution and 300 ml of an aqueous hydrogen chloride (18 wt%) solution. The acidic extract was washed again with 100 ml diethylether and the unified organic fractions were dried over magnesium sulfate. Filtration and evaporation yielded 3.02 (yield: 47 %) of a clear, yellowish oil.

IR(film, cm⁻¹) 2926/2855 (CH₃/CH₂), 1715 (CO), 1639 (C=C), 1461/1375 (CH₃/CH₂), 1265/1169/1101/1023/951

¹H-NMR (250 MHz, CDCl₃, ppm) 1.15-1.36 (m, 15H, CH₂,CH₃), 1.45-1.77 (m, 4H, CH₂), 3.41 (t, 2H, CH₂(3)), 4.03-4.24 (m, 4H, CH₂OPO₃H₂, OCH₂CH₃), 4.11 (s, 2H, CH₂(1)), 5.79 (s, 1H, CH=C), 6.22 (s, 1H, CH=C).

¹³C-NMR (63 MHz, CDCl₃, ppm) 13.98 (CH₃), 25.08, 25.93, 28.92, 29.19, 29.25, 29.30 and 29.45 (CH₂(4-11)), 60.42 (CH₂CH₃), 68.63 and 70.86 (CH₂(1) and CH₂(3)), 125.08 (C=C-CO), 137.38 (C=C-CO), 165.69 (C=C-CO).

Application Example 1 (AG 13-166-1)

0.3052 g N,N'-Bisacrylamido-N,N'-diethyl-1,3-propane, 0.4430 g 3,(4),8,(9)-bis(acrylamido methyl) tricyclo-5.2.1.0^{2,6} decane, 0.1110 g Ethyl 2-[13-dihydrogen phosphoryl-13,2-dioxatridecyl]acrylate, 0.0555 g 2-Acrylamido-2-methyl-propane-sulfonic acid, 0.0067 g camphor quinone, 0.0170 g bis (2,4,6-trimethylbenzoyl)-phenyl phosphine oxide and 0.0078 g dimethylamino benzoic acid ethyl ester were dissolved in a solvent mixture composed of 0.7040 g ethanol and 0.3497 g water.

The following procedure was applied for adhesion measurement to enamel and dentin:

- teeth were abraded by 200 and 500 grit abrasive paper
- teeth were stored at 37 °C in water
- treatment with resin formulation: 20 sec
- evaporation by air stream 5 sec
- light curing 20 sec
- Spectrum TPH body cured on tooth 3 times for 20 sec
- Prepared tooth were stored in water at 37 °C for 2h before measured.

Under these conditions the following values were measured adhesion to dentin: 19.3 ± 1.8 MPa, adhesion to enamel: 15.1 ± 2.2 MPa.

Application Example 2 (FBE-03.96.01)

0.4611 g N,N'-Bisacrylamido-N,N'-diethyl-1,3-propane, 0.3596 g 3,(4),8,(9)-bis(acrylamido methyl) tricyclo-5.2.1.0^{2,6} decane, 0.1320 g Ethyl 2-[5-dihydrogen phosphoryl-5,2-

dioxapentyl]acrylate, 0.1076g 2-Acrylamido-2-methyl-propane-sulfonic acid, 0.0085g camphor quinone, 0.0213 g bis (2,4,6-trimethylbenzoyl)-phenyl phosphine oxide and 0.0099 g dimethylamino benzoic acid ethyl ester were dissolved in a solvent mixture composed of 0.5850 g ethanol and 0.3150 g water.

The following procedure was applied for adhesion measurement to enamel and dentin:

- teeth were abraded by 200 and 500 grit abrasive paper
- teeth were stored at 37 °C in water
- treatment with resin formulation: 20 sec
- evaporation by air stream 5 sec
- light curing 20 sec
- Spectrum TPH body cured on tooth 3 times for 20 sec
- Prepared tooth were stored in water at 37 °C for 2h before measured.

Under these conditions the following values were measured adhesion to enamel: 12.2± 2.3 MPa, adhesion to dentin: 12.7± 2.6 MPa.,

Application Example 3 (FBE-03.90.01)

0.5334 g N,N'-Bisacrylamido-N,N'-diethyl-1,3-propane, 0.4167 g 3,(4),8,(9)-bis(acrylamido methyl) tricyclo-5.2.1.0^{2,6} decane, 0.1076 g 2-Acrylamido-2-methyl-propane-sulfonic acid, 0.0090 g camphor quinone, 0.0227 g bis (2,4,6-trimethylbenzoyl)-phenyl phosphine oxide and 0.0105 g dimethylamino benzoic acid ethyl ester were dissolved in a solvent mixture composed of 0.5850 g ethanol and 0.3150 g water.

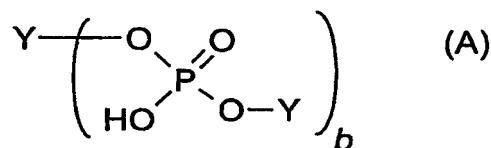
The following procedure was applied for adhesion measurement to enamel and dentin:

- teeth were abraded by 200 and 500 grit abrasive paper teeth were stored at 37 °C in water
- treatment with resin formulation: 20 sec
- evaporation by air stream 5 sec
- light curing 20 sec
- Spectrum TPH body cured on tooth 3 times for 20 sec
- Prepared tooth were stored in water at 37 °C for 2h before measured.

Under these conditions the following values were measured adhesion to enamel: 12.3 ± 3.1 MPa, adhesion to dentin: 11.6 ± 3.1 MPa.

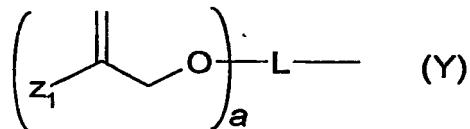
Claims

1. One-part self-etching, self-priming dental adhesive composition having a pH of at most 2, which comprises
 - (a) a polymerizable acidic phosphoric acid ester monomer of the following formula (A):



wherein

the moieties Y independent from each other represent a hydrogen atom or a moiety of the following formula (Y)



wherein

Z_1 is COOR^{10} , COSR^{20} , $\text{CON}(\text{R}^{10})_2$, $\text{CONR}^{10}\text{R}^{20}$, or CONHR^{10} , wherein

R^{10} and R^{20} independently represent

a hydrogen atom,

a C_{1-18} alkyl group optionally substituted by a C_{3-8} cycloalkyl group,

an optionally substituted C_{3-8} cycloalkyl group,

an optionally substituted C_{4-18} aryl or heteroaryl group,

an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group, or

an optionally substituted C_{7-30} aralkyl group,

whereby two R₁ residues may form together with the adjacent nitrogen atom to which they are bound a 5- to 7-membered heterocyclic ring which may contain further nitrogen atoms or an oxygen atoms,
and whereby the optionally substituted groups may be substituted by 1 to 5 C₁₋₅ alkyl group(s);

L represents an (a+b)-valent organic residue (whereby b is 1 when Y in formula (A) is within the round brackets) containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including a + b carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said a+b carbon atoms linking a phosphate or 2-(oxa-ethyl)acryl derivative group;

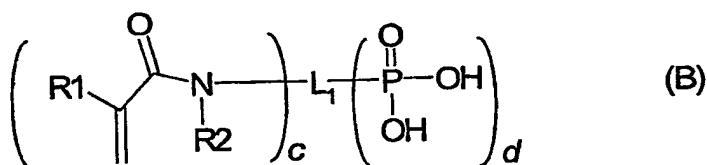
a is an integer of from 1 to 10, preferably 1 to 5;

b is an integer of from 1 to 10, preferably 1 to 5;

provided that at least one Y is not hydrogen; and

(b) one or more polymerisable acidic monomers selected from the group consisting of

(b1) polymerisable acidic monomers of the following formula (B):



wherein

R₁ and R₂ independently represent

a hydrogen atom,

an optionally substituted C₁₋₁₈ alkyl group,

an optionally substituted C₃₋₁₈ cycloalkyl group,

an optionally substituted C₅₋₁₈ aryl or heteroaryl group.

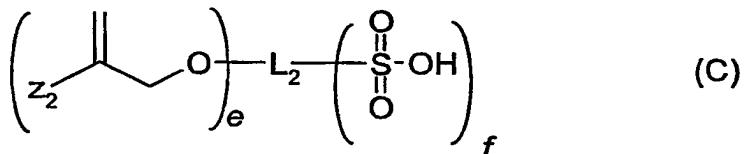
an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group,
 an optionally substituted C_{7-30} aralkyl group,
 whereby the optionally substituted groups may be substituted by 1 to 5
 C_{1-5} alkyl group(s);

L_1 represents a $(c + d)$ valent organic residue containing 2 to 45
 carbon atoms and optionally heteroatoms such as oxygen, nitrogen
 and sulfur, the carbon atoms including $c + d$ carbon atoms selected
 from primary and secondary aliphatic carbon atoms, secondary
 alicyclic carbon atoms, and aromatic carbon atoms, each of said $c+d$
 carbon atoms linking a phosphonate or optionally substituted
 acrylamido group;

and

c and d independently represent integers of from 1 to 10;

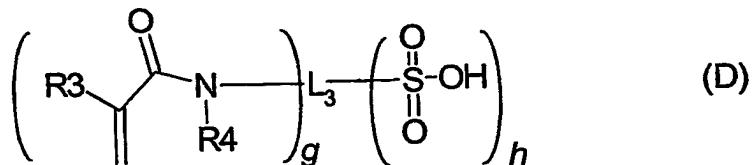
(b2) polymerisable acidic monomers of the following formula (C):



wherein

Z_2 independently has the same meaning as defined for Z_1 ;
 L_2 represents an $(e + f)$ valent organic residue containing 2 to 45 carbon
 atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms,
 the carbon atoms including $e + f$ carbon atoms selected from primary and
 secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and
 aromatic carbon atoms, each of said $e+f$ carbon atoms linking a sulphonate or
 optionally substituted 2-(oxa-ethyl)acryl derivative group; and
 e and f independently represent an integer of from 1 to 10;

(b3) acidic monomers of the following formula (D):



wherein

R_3 and R_4 independently represent

- a hydrogen atom,
- an optionally substituted C_{1-18} alkyl group,
- an optionally substituted C_{3-18} cycloalkyl group,
- an optionally substituted C_{5-18} aryl or heteroaryl group,
- an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group,
- an optionally substituted C_{7-30} aralkyl group,

whereby the optionally substituted groups may be substituted by 1 to 5 C_{1-5} alkyl group(s)

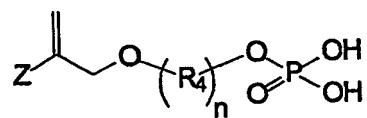
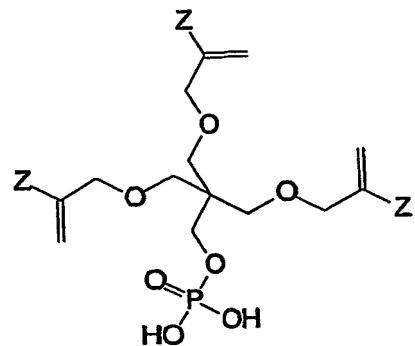
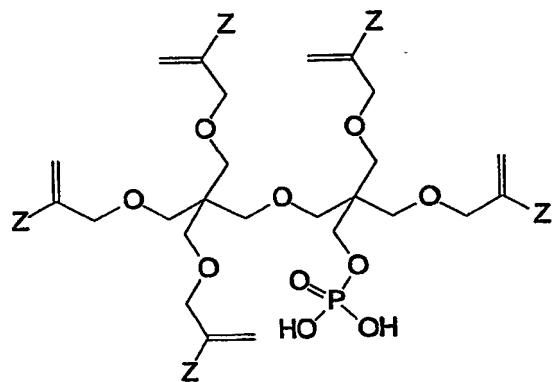
L_3 represents a $(g + h)$ valent valent organic residue containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including $g + h$ carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said $g+h$ carbon atoms linking a sulphonate or optionally substituted acrylamido group; and

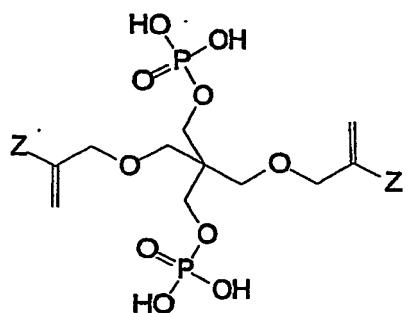
g and h independently represent integers of from 1 to 10;

- (c) a polymerizable N-substituted alkylacrylic or acrylic acid amide monomer;
- (d) an organic and/or inorganic acid;
- (e) an organic water soluble solvent and/or water; and
- (f) polymerization initiator, inhibitor and stabilizer.

2. The one-part self-etching, self-priming dental adhesive composition of claim 1 wherein L₁, L₂, and L₃ independently represent
an optionally substituted C₁₋₁₈ alkylene group which may contain from 1 to 9 oxygen atoms in the chain,
an optionally substituted C₃₋₁₈ cycloalkylene group,
an optionally substituted C₅₋₁₈ arylene or heteroarylene group,
an optionally substituted C₅₋₁₈ alkylaryl or alkylheteroarylene group,
an optionally substituted C₇₋₃₀ aralkylene group.
3. The one-part self-etching, self-priming dental adhesive composition of claim 1 or 2 which is hydrolysis stable for at least one week at a storage temperature of 50 °C, whereby after such storage the bond strength of an adhesive prepared from such an adhesive composition to enamel and/or dentin is at least 10 MPa, preferably 15 MPa.
4. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein components (a) and (b) are contained in a ratio of from 1:100 to 100 : 1.
5. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said organic acid of component (d) is selected from the group of mono- or polycarboxylic acids such as methacrylic acid, acrylic acid, fumaric acid, maleic acid, citric acid, itaconic acid, formic acid and wherein the inorganic acid of component (d) is selected from the group of ethylsulfonic acid, phosphoric acid, sulfuric acid and hydrofluoric acid.
6. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said organic water soluble solvent of component (e) is selected from the group of alcohols and ketones such as ethanol, propanol, butanol, acetone, methyl ethyl ketone.

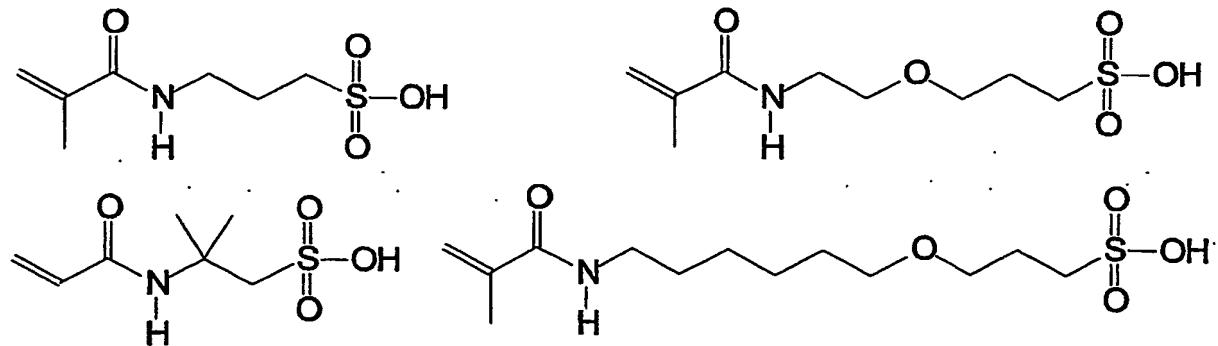
7. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said acidic polymerizable monomer of component (a) is characterized by one of the following formulas:



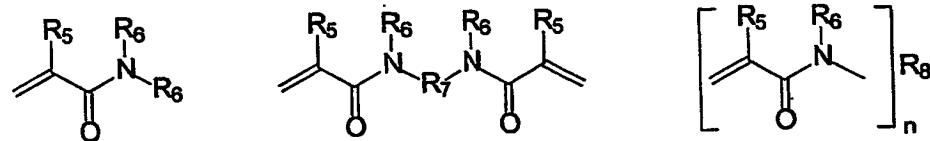


wherein Z is as defined in claim 1 and
 n is an integer.

8. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said acidic polymerizable monomer of component (b) is a polymerisable acidic monomers of formula (C).
9. Hydrolysis stable one-part self-etching, self-priming dental adhesive composition of claim 8, wherein said acidic polymerizable monomer is characterized by one of the following formulas:



10. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein the polymerizable N-substituted alkylacrylic or acrylic acid amide monomer of component (c) is characterized by one of the following formulas:



wherein

R_5 and R_6 independently represent

- a hydrogen atom or a substituted
- a C_1 to C_{18} alkyl group,
- an optionally substituted C_{3-18} cycloalkyl group,
- an optionally substituted C_{5-18} aryl or heteroaryl group,
- an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group,
- an optionally substituted C_{7-30} aralkyl group,

R_7 represents a

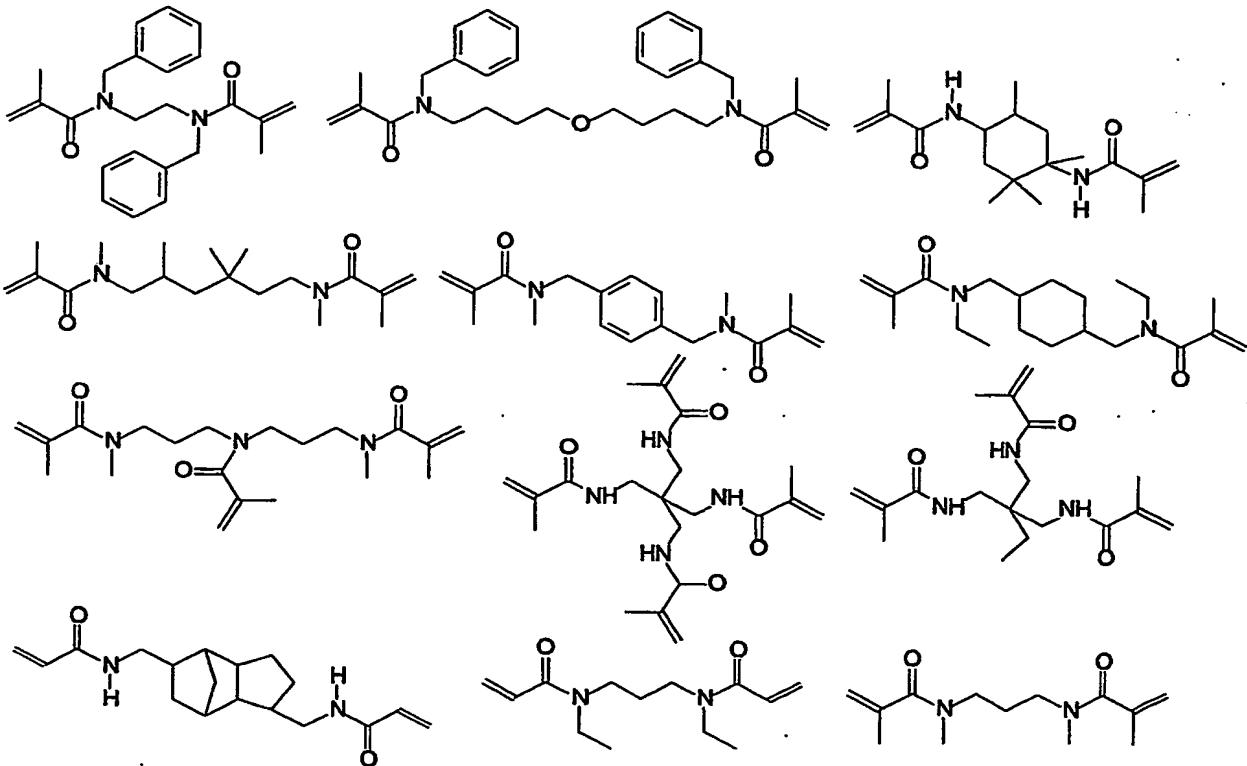
a divalent substituted or unsubstituted organic residue having from 1 to 45 carbon atoms, whereby said organic residue may contain from 1 to 14 oxygen and/or nitrogen atoms and is selected from a C_1 to C_{18} alkylene group wherein from 1 to 6 - CH_2 -groups may be replaced by a $-N(C=O)-CR_9=CH_2$ group wherein R_9 is a hydrogen atom or a C_1 to C_{18} alkyl group, a divalent substituted or unsubstituted C_3 to C_{18} cycloalkyl or cycloalkylene group, a divalent substituted or unsubstituted C_4 to C_{18} aryl or heteroaryl group, a divalent substituted or unsubstituted C_5 to C_{18} alkylaryl or alkylheteroaryl group, a divalent substituted or unsubstituted C_7 to C_{30} aralkyl group, and a divalent substituted or unsubstituted C_2 to C_{45} mono-, di- or polyether group having from 1 to 14 oxygen atoms,

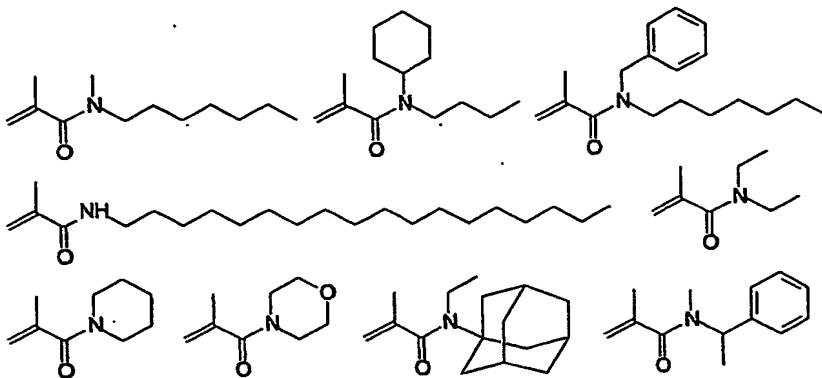
R_8 represents

a saturated di- or multivalent substituted or unsubstituted C₂ to C₁₈ hydrocarbon group, a saturated di- or multivalent substituted or unsubstituted cyclic C₃ to C₁₈ hydrocarbon group, a di- or multivalent substituted or unsubstituted C₄ to C₁₈ aryl or heteroaryl group, a di- or multivalent substituted or unsubstituted C₅ to C₁₈ alkylaryl or alkylheteroaryl group, a di- or multivalent substituted or unsubstituted C₇ to C₃₀ aralkyl group, or a di- or multivalent substituted or unsubstituted C₂ to C₄₅ mono-, di-, or polyether residue having from 1 to 14 oxygen atoms, and

n is an integer.

11. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said polymerizable monomer is a mono-, bis- or poly(meth) acrylamide characterized by one of the following formulas:





12. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, which contains said acidic polymerizable monomers of components (a) and (b) in an amount of from 5 to 90 wt-%.
13. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said polymerization initiator is a thermal initiator, a redox-initiator or a photo initiator.
14. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said photo initiator is champhor quinone.
15. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said filler is an inorganic filler and/or an organic filler; preferably the filler is a nanofiller.
16. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said stabilizer is a radical absorbing monomer such as hydroquinone, hydroquinone monomethylether, 2,6-di-tert.-butyl-p-cresol.
17. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein L represents

an (a+b)-valent saturated aliphatic C₂ to C₁₈ group having at least 2 of said primary aliphatic carbon atoms, and optionally 1 or more of said secondary aliphatic carbon atom(s), whereby said (a+b)-valent group may be substituted by C₁ to C₅ alkyl group(s); or

a C₂ to C₄₅ mono-, di-, or polyether which has from 1 to 14 oxygen atoms and is substituted by at least 2 C₁ to C₁₀ aliphatic group(s) having said primary and/or secondary aliphatic carbon atoms; whereby said ether may optionally be substituted by C₁ to C₅ alkyl group(s); or

wherein L represents:

a saturated C₃ to C₈ cyclic, C₇ to C₁₅ bi- or polycyclic hydrocarbon group having from 0 to 4, preferably, 0 to 3, more preferably 0 or 1, of said secondary alicyclic carbon atoms; and/or

a C₄ to C₁₈ aryl or heteroaryl group having from 0 to 5, preferably 0 to 3, more preferably 0 or 1, of said aromatic carbon atoms; whereby said saturated hydrocarbon or aryl or heteroaryl group is substituted by from 0 to 5 C₁ to C₅ alkyl group(s);

from 0 to 4, preferably 1 to 3, more preferably 1 or 2, saturated C₁ to C₁₀ aliphatic group(s) having said primary and/or secondary aliphatic carbon atoms, and/or

from 0 to 2 divalent residues according to one of the following formulas:

-[O-CH₂CH₂-]_f wherein f is an integer of from 1 to 10, preferably 1 to 5;

-[-O-CH₂CH₂CH₂-]_g- wherein g is an integer offrom 1 to 10, preferably 1 to 5;

-[O-R₁₂]_h- wherein R₁₂ is -CH(CH₃)-CH₂- or -CH₂-CH(CH₃)- and h is an integer of from 1 to 10, preferably 1 to 5;

-[-O-R₁₄]_i-[-O-R₁₅]_j- or -[-O-R₁₅]_k-[-O-R₁₄]_l- wherein R₁₄ is -CH₂CH₂-, R₁₅ is -CH(CH₃)-CH₂- or -CH₂-CH(CH₃)-, i, j, k, and l are integers whereby

2i + 3j ≤ 15 and 2k + 3l ≤ 15,

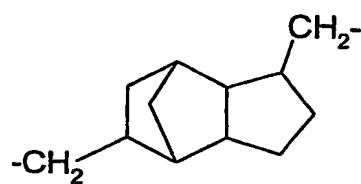
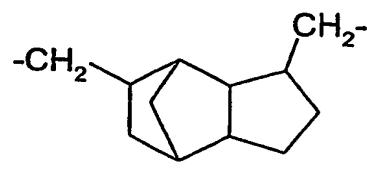
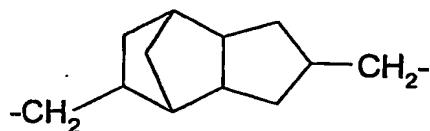
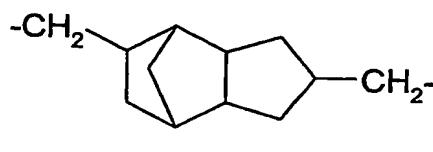
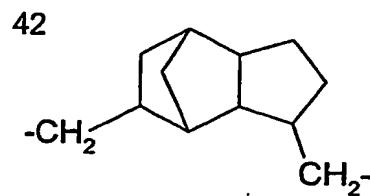
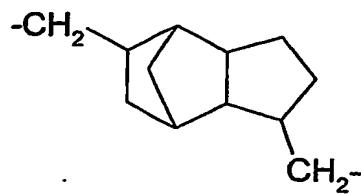
-[-O-CH₂CH₂CH₂CH₂-]_r- wherein r is an integer of 1 or 2;

wherein said divalent residues have one of said primary aliphatic carbon atoms; and

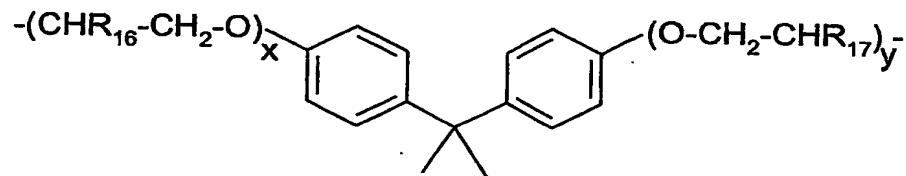
whereby 2 groups selected from said saturated hydrocarbon, aryl, and heteroaryl groups may optionally be linked by a single bond, an alkylene group, or -O-.

18. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein L represents an (a+b)-valent saturated C₃ to C₈ cyclic or C₇ to C₁₅ bi- or tricyclic hydrocarbon group having at least 2 of said secondary alicyclic carbon atoms; an (a+b)-valent saturated C₄ to C₁₈ aryl or heteroaryl group having from 2 to 6 of said aromatic carbon atoms; an (a+b)-valent C₆ to C₁₈ alkylaryl or alkyl heteroaryl group having at least one of said aromatic carbon atoms, at least one of said secondary aliphatic carbon atoms, and optionally one of said primary aliphatic carbon atoms at the terminal end of the alkyl moiety of said alkylaryl or alkylheteroaryl group; or an (a+b)-valent C₈ to C₃₀ aralkyl group having at least one of said primary aliphatic carbon atoms and at least one of said secondary aliphatic carbon atoms.

19. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein L represents is a divalent residue according to one of the following formulas:
 -[CH₂CH₂-O-]_m-CH₂CH₂- wherein m is an integer of from 1 to 14,
 -[CH₂CH₂ CH₂-O-]_p-CH₂CH₂ CH₂- wherein p is an integer of from 1 to 14,
 -[R₁₂-O]_q-R₁₃- wherein R₁₂ and R₁₃ may be -CH(CH₃)-CH₂- or -CH₂-CH(CH₃)- and q is from 1 to 14,
 -[R₁₄-O]_r-[R₁₅-O]_s-R₁₄- or -[R₁₄-O]_r-[R₁₅-O]_u-R₁₅- wherein R₁₄ is -CH₂CH₂-, R₁₅ is -CH(CH₃)-CH₂- or -CH₂-CH(CH₃)-, r, s, t, and u are integers whereby 2r + 3s ≤ 43 and 2t + 3u ≤ 42,
 -[CH₂CH₂CH₂CH₂-O-]_r-CH₂CH₂CH₂CH₂- wherein r is 1 or 2,

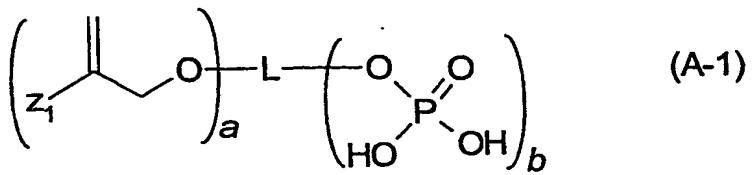


or



wherein R₁₆ and R₁₇ are H or -CH₃ and x and y may independently be integers of from 0 to 10, preferably 0 to 5.

20. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims, wherein said (a+b) carbon atoms are primary aliphatic carbon atoms.
21. The one-part self-etching, self-priming dental adhesive composition according to any one of the preceding claims wherein the polymerizable acidic phosphoric acid ester monomer is of the following formula (A-1):



wherein

Z_1 is COOR^{10} , COSR^{20} , $\text{CON}(\text{R}^{10})_2$, $\text{CONR}^{10}\text{R}^{20}$, or CONHR^{10} , wherein R^{10} and R^{20} independently represent

a hydrogen atom,

a C_{1-18} alkyl group optionally substituted by a C_{3-8} cycloalkyl group,

an optionally substituted C_{3-8} cycloalkyl group,

an optionally substituted C_{4-18} aryl or heteroaryl group,

an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group, or

an optionally substituted C_{7-30} aralkyl group,

whereby two R_1 residues may form together with the adjacent nitrogen atom to which they are bound a 5- to 7-membered heterocyclic ring which may contain further nitrogen atoms or an oxygen atoms,

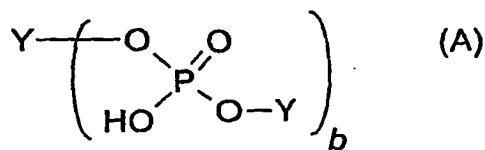
and whereby the optionally substituted groups may be substituted by 1 to 5 C_{1-5} alkyl group(s);

L represents an $(a+b)$ -valent organic residue containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including $a + b$ carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said $a+b$ carbon atoms linking a phosphate or 2-(oxa-ethyl)acryl derivative group;

a is an integer of from 1 to 10, preferably 1 to 5;

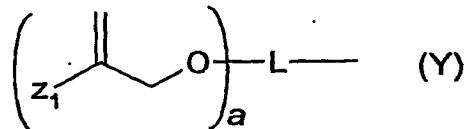
b is an integer of from 1 to 10, preferably 1 to 5.

22. The one-part self-etching, self-priming dental adhesive composition according to any one of claims 1 to 20 wherein none of the moieties Y is a hydrogen atom.
23. A polymerizable acidic phosphoric acid ester monomer of the following formula (A)



wherein

the moieties Y independent from each other represent
a moiety of the following formula (Y)



wherein

Z_1 is COOR^{10} , COSR^{20} , $\text{CON}(\text{R}^{10})_2$, $\text{CONR}^{10}\text{R}^{20}$, or CONHR^{10} , wherein

R^{10} and R^{20} independently represent

a hydrogen atom,

a C_{1-18} alkyl group optionally substituted by a C_{3-8} cycloalkyl group,

an optionally substituted C_{3-8} cycloalkyl group,

an optionally substituted C_{4-18} aryl or heteroaryl group,

an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group, or

an optionally substituted C_{7-30} aralkyl group,

whereby two R₁ residues may form together with the adjacent nitrogen atom to which they are bound a 5- to

7-membered heterocyclic ring which may contain further nitrogen atoms or an oxygen atoms,

and whereby the optionally substituted groups may be substituted by 1 to 5 C₁₋₅ alkyl group(s);

L represents an (a+b)-valent organic residue (whereby b is 1 when Y in formula (A) is within the round brackets) containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including a + b carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said a+b carbon atoms linking a phosphate or 2-(oxa-ethyl)acryl derivative group;

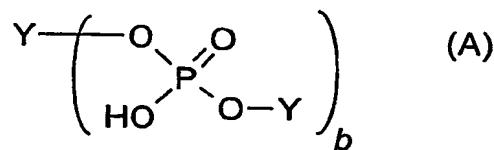
a is an integer of from 1 to 10, preferably 1 to 5;

b is an integer of from 1 to 10, preferably 1 to 5, more preferably 1.

ABSTRACT**23. Dez. 2003**

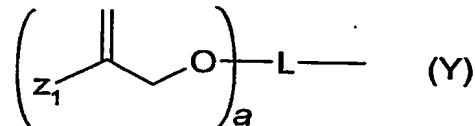
One-part self-etching, self-priming dental adhesive composition having a pH of at most 2, which comprises

- (a) a polymerizable acidic phosphoric acid ester monomer of the following formula (A):



wherein

the moieties Y independent from each other represent a hydrogen atom or a moiety of the following formula (Y)



wherein

Z_1 is COOR^{10} , COSR^{20} , $\text{CON}(\text{R}^{10})_2$, $\text{CONR}^{10}\text{R}^{20}$, or CONHR^{10} , wherein

R^{10} and R^{20} independently represent

a hydrogen atom,

a C_{1-18} alkyl group optionally substituted by a C_{3-8} cycloalkyl group,

an optionally substituted C_{3-8} cycloalkyl group,

an optionally substituted C_{4-18} aryl or heteroaryl group,

an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group, or

an optionally substituted C_{7-30} aralkyl group,

whereby two R₁ residues may form together with the adjacent nitrogen atom to which they are bound a 5- to 7-membered heterocyclic ring which may contain further nitrogen atoms or an oxygen atoms,

and whereby the optionally substituted groups may be substituted by 1 to 5 C₁₋₅ alkyl group(s);

L represents an (a+b)-valent organic residue (whereby b is 1 when Y in formula (A) is within the round brackets) containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including a + b carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said a+b carbon atoms linking a phosphate or 2-(oxa-ethyl)acryl derivative group;

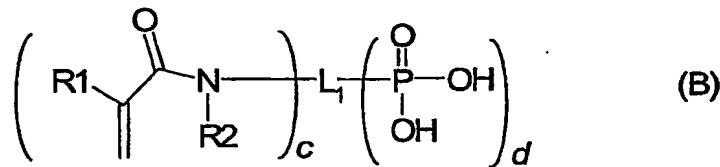
a is an integer of from 1 to 10, preferably 1 to 5;

b is an integer of from 1 to 10, preferably 1 to 5;

provided that at least one Y is not hydrogen; and

(b) one or more polymerisable acidic monomers selected from the group consisting of

(b1) polymerisable acidic monomers of the following formula (B):



wherein

R₁ and R₂ independently represent

a hydrogen atom,

an optionally substituted C₁₋₁₈ alkyl group,

an optionally substituted C₃₋₁₈ cycloalkyl group,

an optionally substituted C₅₋₁₈ aryl or heteroaryl group,

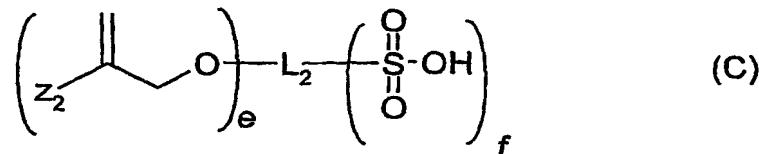
an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group,
 an optionally substituted C_{7-30} aralkyl group,
 whereby the optionally substituted groups may be substituted by 1 to 5
 C_{1-5} alkyl group(s);

L_1 represents a $(c + d)$ valent organic residue containing 2 to 45
 carbon atoms and optionally heteroatoms such as oxygen, nitrogen
 and sulfur, the carbon atoms including $c + d$ carbon atoms selected
 from primary and secondary aliphatic carbon atoms, secondary
 alicyclic carbon atoms, and aromatic carbon atoms, each of said $c+d$
 carbon atoms linking a phosphonate or optionally substituted
 acrylamido group;

and

c and d independently represent integers of from 1 to 10;

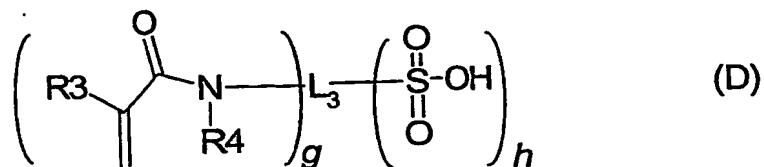
(b2) polymerisable acidic monomers of the following formula (C):



wherein

Z_2 independently has the same meaning as defined for Z_1 ;
 L_2 represents an $(e + f)$ valent organic residue containing 2 to 45 carbon
 atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms,
 the carbon atoms including $e + f$ carbon atoms selected from primary and
 secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and
 aromatic carbon atoms, each of said $e+f$ carbon atoms linking a sulphonate or
 optionally substituted 2-(oxa-ethyl)acryl derivative group; and
 e and f independently represent an integer of from 1 to 10;

(b3) acidic monomers of the following formula (D):



wherein

R_3 and R_4 independently represent

- a hydrogen atom,
- an optionally substituted C_{1-18} alkyl group,
- an optionally substituted C_{3-18} cycloalkyl group,
- an optionally substituted C_{5-18} aryl or heteroaryl group,
- an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group,
- an optionally substituted C_{7-30} aralkyl group,

whereby the optionally substituted groups may be substituted by 1 to 5 C_{1-5} alkyl group(s)

L_3 represents a $(g + h)$ valent valent organic residue containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including $g + h$ carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said $g+h$ carbon atoms linking a sulphonate or optionally substituted acrylamido group; and

g and h independently represent integers of from 1 to 10;

- (c) a polymerizable N-substituted alkylacrylic or acrylic acid amide monomer;
- (d) an organic and/or inorganic acid;
- (e) an organic water soluble solvent and/or water; and
- (f) polymerization initiator, inhibitor and stabilizer.

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